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01MAR04 E877074-6 D02806
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1. Your reference — CDK2160

2. Patent application number *(The Patent Office will fill in this part)* — 0404481.4

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

RHODIA CONSUMER SPECIALTIES LIMITED
Oak House, Reeds Crescent, Watford,
Hertfordshire, WD24 4QP

07810322006
Patents ADP number *(if you know it)*

28 FEB 2004

If the applicant is a corporate body, give the country/state of its incorporation — England

4. Title of the invention — SOAP CONTROL AGENT

5. Name of your agent *(if you have one)* — Barker Brettell

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

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B16 9PW

Patents ADP number *(if you know it)* — 7442494002

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Country	Priority application number *(if you know it)*	Date of Filing *(day/month/year)*

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8. Is a Patents Form 7/77 (Statement of inventorship and of right to grant of a patent) required in support of this request? *Answer 'Yes' if:*
a) any applicant named in part 3 is not an inventor, or
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Continuation sheets of this form	-
Description	7 + 7
Claim(s)	5 + 5
Abstract	-
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Priority documents	-
Translations of priority documents	-
Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	-
Request for preliminary examination *(Patents Form 9/77)*	1
Request for substantive examination *(Patents Form 10/77)*	-
Any other documents *(please specify)*	-

11. I/We request the grant of a patent on the basis of this application.

Signature: Barker Brettell — Date: 27 February 2004

12. Name and daytime telephone number of person to contact in the United Kingdom: Lucy P. Trueman — Tel: 0121 456 1364

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SOAP CONTROL AGENT

This invention relates to phosphonated polymers as naphthenate and carboxylate salt control agents, the use of such agents and the method of use of such agents.

Crude oil invariably contains naphthenic and carboxylic/fatty acids in varying amounts dependent upon the source of the crude oil.

When crude oil contacts an aqueous phase, for example reservoir water, it is possible for metal salts of naphthenic and fatty acids to be formed. The metal ions in the aqueous phase can react with carboxylic groups on the acids to form salts (these are typically referred to as soaps).

These soaps can be very problematic during oil recovery and downstream processing. Typical problems include:

- the formation of oil water sludge and emulsions which hinder oil water separation processes;
- the formation of hard scales which cause retardation of fluid flow, block processing equipment and reduce the quality of the oil;
- soluble metal soaps remaining in the crude oil during the separation process and accordingly the crude oil contains residual levels of metal ions such as calcium, magnesium and iron;
- the presence of metal ions reducing the value of the crude oil; and

- the presence of metal ions also causing processing problems as soaps can deposit in preheat trains and decompose during resid conversion, hydroconversion or coking procedures.

Currently, naphthenate and carboxylate soap formation is treated by the addition of large volumes of acetic acid. However, this type of treatment suffers from volumes of acetic acid being needed and high corrosion rates that are experienced as a result of using acetic acid.

The present invention aims to ameliorate the above disadvantages by providing a non-corrosive treatment that can effectively control naphthenate and carboxylate soap formation during oil recovery and processing operations.

Accordingly, the present invention provides a soap control agent comprising a phosphorus containing polymer.

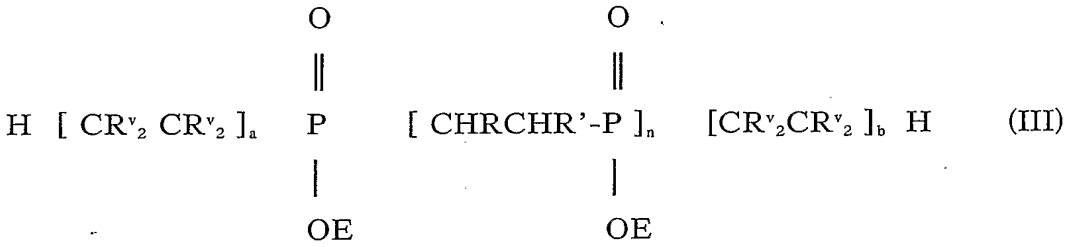
The phosphorus containing polymer may have a phosphonate or phosphinate end cap. The end capped polymer is of formula (I)

$X_2O_3PCHYCZ_2PO_2XR$ (I)

wherein X is H or an alkali metal, alkaline earth or other polyvalent metal, ammonium or an organic base, and R is a polymeric chain comprising between 1 and 100,000 groups, said group or groups being derived from at least 1 unsaturated compound in which the multiple bond is activated chemically by an adjacent electron withdrawing group, and Y and Z are each hydrogen, a PO_3A_2, SO_3A or CO_2A group wherein A is hydrogen or an alkyl or aryl moiety.

R is preferably a polymer of acrylic acid. Alternatively, R is a polymer of a carboxylic or sulphonic acid, e.g. methacrylic acid, maleic acid, vinyl sulphonic acid or 2-acrylamido-2-methylpropane sulphonic acid. R may also be a copolymer of VPA (vinyl phosphonic acid) and VDPA (vinyl diphosphonic acid).

Alternatively, the phosphorus containing polymer is a telomer of formula (III):



(III)

wherein E is hydrogen or a cation, R and R' are each independently selected from the group consisting of hydrogen, hydroxyl, carboxyl, alkyl, aryl, alkaryl, hydroxy-substituted alkyl, aryl or alkaryl and carboxy-substituted alkyl, aryl or alkaryl, provided that R and R' together have a total of less than 23 carbon atoms,

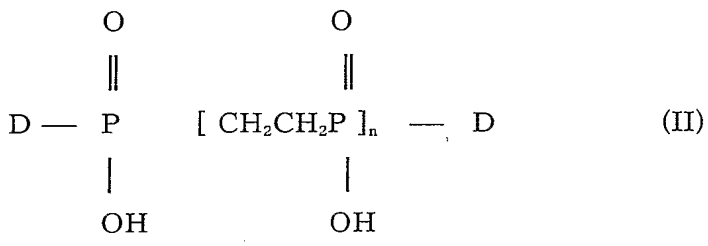
at least one R^v in each monomer unit is selected from the group consisting of hydroxy, carboxy, sulpho, phosphono, amido, aceto, aryl and halogen;

each other R^v is independently selected from the group consisting of hydrogen, C_{1-4} alkyl, carboxyl, sulpho, phosphono, hydroxyl groups, carboxy-substituted, sulpho-substituted, phosphono-substituted and hydroxy-substituted C_{1-4} alkyl groups;

(a+b) is in the range 5 to 200 and n is greater than 1.

The telomer of formula (III) is preferably produced by co-polymerising a polymer of formula II (below) with at least one monomer of formula $CR_2^v = CR_2^v$, wherein R^v has the same meaning as above.

Formula (II) is:



(II)

wherein D is hydrogen or a cation or an alkyl group and n is 1.05 to 100.

The present invention, in a second aspect, provides the use of a soap control agent as defined in the first aspect to remove metal ions from a medium.

The medium is preferably crude oil. Alternatively, the medium is a mixture, in an proportion, of hydrocarbons containing naphthenic or fatty acids with water. In particular, the water can be injection water, reservoir water (connate water) or water from oil fields, or any system where water contact or is in contact with crude oil or naphthenic acid or fatty acid containing fluids.

Furthermore, the medium can be selected from processed soaps and cleaning formulations as used in personal home care applications.

The present invention in a third aspect, provides a method of removing metal ions from a medium comprising contacting the medium with an

effective amount of phosphorus containing polymer in accordance with the first aspect of the invention.

The medium is preferably crude oil. Alternatively, the medium is a mixture, in any proportion, of hydrocarbons containing naphthenic or fatty acids with water. In particular, the water can be injection water, reservoir (connate water) or produced water from oil fields, or any system water or in contact with crude oil or naphthenic acid or fatty acid containing fluids. Furthermore, the medium can be processed soaps and cleaning formulations as used in personal homecare applications.

The soap control agent is used in an effective amount of between 0.01 to 100,000ppm. Preferably the soap control agent is used in an effective amount of between 1 to 10,000ppm.

The soap is selected from the group consisting of calcium naphthenate, magnesium naphthenate, iron naphthenate, calcium carboxylate, magnesium carboxylate and iron carboxylate.

The metal ions are preferably selected from the group consisting of Mg^{2+}, Ca^{2+}, Fe^{2+}/Fe^{3+}.

It will be appreciated that the use of the soap control agent according to the invention is not to be limited to soap control in crude oil. The soap control agent may be used in other areas where soap control is important, for example, laundry detergents and domestic cleaning products.

It is believed that the soap control agents work by sequestering metal ions. Once the metal ions have been sequestered, soap formation is inhibited. It is also believed that the polymers in accordance with the

invention interact with soaps to destabilise them. This is, of course, a theory and should not be construed as being limiting or factual.

It is advantageous that the use of phosphonated polymers in accordance with the present invention control soap formation with no emulsification of the oil-water systems.

The present invention will now be described, with reference to the following example

Example 1

Potential soap control agents were added to 70mls of a crude oil, previously characterised as containing 50ppm Ca, at a treatment level of 500ppm product. The treated crude oil was stored at 60°C for 2 hours. The crude oil was washed with 30mls of de-ionised water to remove any water-soluble calcium compounds from the oil. The "washing" was processed to remove residual oil. The processed washings were then analysed for calcium content using ICPES (inductively coupled plasma emission spectroscopy).

Effective soap control agents will scavenge the calcium from the crude oil and migrate into the de-ionised water. Therefore, the efficacy of the soap control agent is directly proportional to the amount of calcium in the processed washings.

The results are summarised below:

Soap control agent evaluated Evaluated	**ppm Calcium in deionised water after extraction**
Control (de-ionised water)	14
Long chain mono-phosphonic acid	2
Oil soluble phosphonocarboxylate	5
HEDP – conventional phosphonate	6
Long chain di-phosphonic acid	6
Dialkyl alkyl phosphonate	11
Short chain phosphonocarboxylate	21
Phosphonate end capped polymer I	57
Short chain phosphine oxide	29
Acetic acid	32
P-Block polymer	60
Phosphonate end capped polymer II	61

This table shows that the novel phosphorus containing compounds (phosphonate end capped polymer I, P-block polymer and phosphonate end capped polymer II), in accordance with the invention, effectively decrease the amount of metal ions in crude oil and thereby inhibit soap formation and alleviate the problems associated with soaps in crude oil.

CLAIMS

1. A soap control agent comprising a phosphorus containing polymer.

2. A soap control agent as claimed in claim 1 in which the phosphorus containing polymer has a phosphonate or phosphinate end cap.

3. A soap control agent as claimed in claim 2 in which the end cap polymer is of formula 1.

$X_2O_3PCHYCZ_2PO_2XR$ (I)

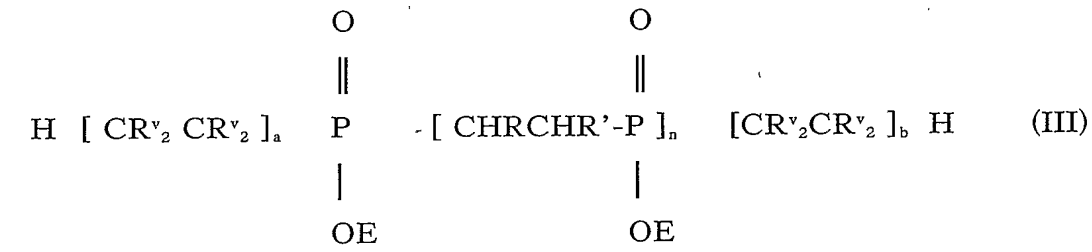
wherein X is H or an alkali metal, alkaline earth or other polyvalent metal, ammonium or an organic base, and R is a polymeric chain comprising between 1 and 100,000 groups, said group or groups being derived from at least 1 unsaturated compound in which the multiple bond is activated chemically by an adjacent electron withdrawing group, and Y and Z are each hydrogen, a PO_3A_2, SO_3A or CO_2A group wherein A is hydrogen or an alkyl or aryl moiety.

4. Soap control agent as claimed in claim 3 in which R is a polymer of acrylic acid.

5. A soap control agent as claimed in claim 3 in which R is a polymer of a carboxylic or sulphonic acid selected from the group consisting of methacrylic acid, maleic acid, vinyl sulphonic acid and 2-acrylamido-2-methylpropane sulphonic acid.

6. A soap control agent as claimed in claim 3 in which R is copolymer of VPA (vinyl phosphonic acid) and VDPA (vinyl diphosphonic acid)

7. A soap control agent as claimed in claim 1 in which the phosphorus containing polymer is a telomer of formula (III):



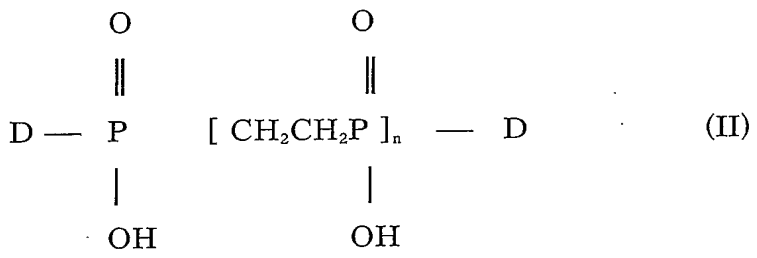
(III)

Wherein E is hydrogen or a cation, R and R' are each independently selected from the group consisting of hydrogen, hydroxyl, carboxyl, alkyl, aryl, alkaryl, hydroxy-substituted alkyl, aryl or alkaryl and carboxy-substituted alkyl, aryl or alkaryl, provided that R and R' together have a total of less than 23 carbon atoms, at least one R^v in each monomer unit is selected from the group consisting of hydroxy, carboxy, sulpho, phosphono, amido, aceto, aryl and halogen;

each other R^v is independently selected from the group consisting of hydrogen, C_{1-4} alkyl, carboxyl, sulpho, phosphono, hydroxyl groups, carboxy-substituted, sulpho-substituted, phosphono-substituted and hydroxy-substituted C_{1-4} alkyl groups;

(a+b) is in the range 5 to 200 and n is greater than 1.

8. A soap control agent as claimed in claim 1 or claim 7 in which the telomer of formula (III) is produced by co-polymerising a polymer of formula II with at least one monomer of formula $CR_2^v = CR_2^v$, wherein R^v has the same meaning as in claim 7 and wherein formula (II) is :



(II)

wherein D is hydrogen or a cation or an alkyl group and n is 1.05 to 100.

9. The use of a soap control agent as defined any of claims 1 to 8 to remove metal ions from a medium.

10. The use of a soap control agent as claimed in claim 9 in which the medium is crude oil.

11. The use of a soap control agent as claimed in claim 9 in which the medium is a mixture, in any proportion, of hydrocarbons containing naphthenic or fatty acids with water.

12. The use as claimed in claim 11 in which the water is injection water, reservoir water (connate water) water from oil fields, or water from any system where water contacts or is in contact with crude oil or naphthenic acid or fatty acid containing fluids.

13. The use as claimed in claim 9 in which the medium is selected from process soaps and cleaning formulations used in personal home care applications.

14. The use as claimed in any one of claims 9 to 13 in which the metal ions are selected from Mg^{2+}, Ca^{2+}, Fe^{2+}/Fe^{3+}.

15. A method of removing metal ions from a medium comprising contacting the medium with an effective amount of phosphorus containing polymer in accordance with the first aspect of the invention.

16. A method of removing metal ions as claimed in claim 15 in which the medium is crude oil

17. A method of removing metal ions as claimed in claim 15 in which the medium is a mixture, in any proportion, of hydrocarbons containing naphthenic or fatty acids with water.

18. A method of removing metal ions as claimed in claim 17 in which the water is selected from the group consisting of injection water, reservoir water (connate water), water from oil fields, or water from any system contacting or in contact with crude oil or naphthenic acid or fatty acid containing fluids.

19. A method of removing metal ions as claimed in claim 15 in which the medium is selected from processed soaps and cleaning formulations as used in personal home care applications.

20. A method of removing metal ions as claimed in any one of claims 15 to 19 in which the effective amount is between 0.01 to 10,000 ppm.

21. A method of removing metal ions from a medium to control soap information in which the soap is selected from the group consisting of calcium naphthenate, magnesium naphthenate, iron naphthenate, calcium carboxylate, magnesium carboxylate and iron carboxylate.

22. A method of removing metal ions as claimed in any one of claims 15 to 21 in which the metal ions are selected from the group consisting of Mg^{2+}, Ca^{2+}, Fe^{2+}/Fe^{3+}.

23. A soap control agent substantially as disclosed herein and with reference to the accompanying example.

24. A method of removing metal ions substantially as described herein and with reference to the accompanying example.

25. The use of a soap control agent substantially as described herein and with reference to the accompanying example.

26. A method of removing metal was from a medium to control soap formation substantially as described herein with reference to the accompanying example.